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Raman spectroscopy and microhardness of ion-implanted a-C:H-films

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Abstract

Optical and mechanical properties of a-C:H films subjected to carbon or nitrogen ion implantation ($E = 150$ keV, $D = 1.10^{13}$–1.10^{17} cm^{-2}) were studied. A correlation between hardness and Raman spectrum parameters of the films has been ascertained. After intermediate dose ion implantation ($\sim 10^{16}$ cm^{-2}) a drastic increasing of hardness and Young's modulus of implanted films was observed. High dose implantation (10^{17} cm^{-2}) results in appearance of structural inhomogeneities in the implanted region having extremely high hardness. The possible mechanisms of the effects observed are explained from the comparison of Raman and hardness data. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Microhardness; A. Films; A. Implantation; B. Spectroscopy

1. Introduction

Ion-implantation is a powerful tool for controllable modification of material properties. The possibility to control the ion energy and, as a result, the ion penetration depth is especially important for film modification. There is substantial literature devoted to ion-beam induced carbon film modification. Among the results obtained for implanted a-C, a-C:H, and a-C:H:N films the following deserve most attention.

The improvement of wear resistance of GC implanted with nitrogen, helium, carbon, oxygen, neon or argon ions was observed [1]. The effect mentioned is stipulated by disordering and ion-beam induced compaction of GC [1–3]. Ion-beam induced compaction was also observed for GC implanted with C^+ ions [4]. In this case an increase of refractive index of irradiated GC was also found [4]. It is the authors opinion that the effects mentioned are connected by ion-beam induced disordering of GC being accompanied by conversion of a part of sp^2-coordinated bonds into sp^3-coordinated ones. This conclusion is also confirmed by the appearance of an optical bandgap in GC after "hot" carbon implantation [5]. Compaction of GC under action of nitrogen implantation leads at some doses (up to 5.10^{17} cm^{-2}) to appearance of a step on the film surface between implanted and unimplanted regions [6]. The height of the step is a function of implantation dose and can be as large as ~2000 A. The authors also observed the appearance of linear surface features at a dose of 5.10^{17} cm^{-2}. Similar surface features observed in DLC films have been attributed to stress relief [7]. It is evident that to investigate such local features an experimental technique with high surface resolution should be used.

For nitrogen implanted carbon films the most interesting results are the formation of C–N bonds in a-C films [8], the decrease of internal stresses in a-C:H and a-C:H:N [9], and significant an increase of hardness of "soft" a-C:H and a-C [5,10] films after nitrogen implantation. Taking into account the above mentioned results it seems worthwhile to compare the effect of nitrogen and carbon implantation on a-C:H film properties.

The aim of this work was to investigate the properties of a-C:H films implanted with nitrogen or carbon ions. Particular attention has been paid to the study of ion implanted film hardness spatial distribution and local features of the films subjected to high dose implantation.

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The investigations were carried out by high spatial resolution micro-Raman and nanoindentation techniques.

2. Experimental

The a-C:H films used in this study were deposited by RF (13.56 MHz) plasma decomposition of CH_4:H_2 gas mixture in a parallel plate reactor. The total pressure in the reaction chamber was 0.6 Torr. Si (100) and quarz wafers were used as the substrates. During the deposition process the substrates were maintained at room temperature and fixed RF bias voltage (from 1200 to 1900 V). The thickness of the films was 1200 nm.

Carbon and nitrogen implantation was performed at an ion energy of 150 keV and with doses from 1.10^{13} to 3.10^{16} cm^{-2}. Some of the a-C:H films deposited onto the Si substrate were implanted by nitrogen ions with doses up to 1.10^{17} cm^{-2}. The ion beam current density did not exceed 3 mkA/cm^2.

The mechanical properties of the films were studied using a microanalyzer ("Nano Indenter II", Nano Instruments Inc., Knoxville, TN, USA) at various loadings and, as a result, at different penetration depths of indenter (PDI). A Bercovich's indenter was used. The accuracy of the indenter positioning on the sample surface was 0.4 μm. The mean value of film hardness was determined by averaging the results of 10 tests.

Raman scattering measurements were performed in a backscattering configuration with a Jobin-Yvon T64000 spectrometer coupled with an Olympus metallographic microscope. Both the excitation and collection of the light were performed through the microscope objective. The excitation was made using the 488 nm line of an argon laser. The spot size on the sample is given by 1.22*λ/NA. For the objective used (×100, NA = 0.95), this gives a value of about 0.63 μm. The excitation laser power on the sample was in the range 0.26–2.25 mW. All measurements were made at room temperature.

3. Results and discussion

Fig. 1 shows Raman spectra (RS) of a-C:H films implanted by carbon and nitrogen ions with the dose of 1.10^{16} cm^{-2}. Two bands at ~1590 and ~1360 cm^{-1} are observed which are characteristic for amorphous carbon films and are usually denoted as *G*- ("graphitic"- at 1590 cm^{-1}) and *D*- ("disordered"-at 1360 cm^{-1}) bands [1,2,11]. It should be noted that the RS of all implanted films were similar to the spectra presented in Fig. 1. The spectrum of initial (unimplanted) film was characterized by the presence of a broad luminescence band in addition to *G*− and *D*− Raman bands. Disappearance of luminescence background in Raman spectra from the implanted films (Fig. 1) and broadening of *D*− and *G*−bands are stipulated by ion-beam induced film disordering. As a result of implantation the centers of nonradiative recombination, such as dangling bonds, appear and cause the quenching of the luminescence. Before fitting the initial film RS with elementary bands the luminescence baseline correction was carried out. As a result of the fitting procedure the ratio of *D*− and *G*−band integral intensity (I_D/I_G) has been determined for all investigated films. It is well known that I_D/I_G value accounts for the amount of sp^2- distorted and undistorted bonds in an amorphous carbon film [1,2,11].

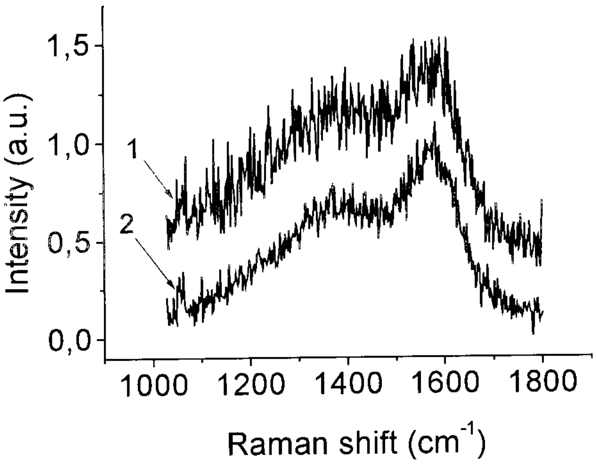

Fig. 1. Raman spectra of carbon (1) and nitrogen (2) implanted films (1.10^{16} cm^{-2}).

The hardness and I_D/I_G dose dependences for the films implanted by carbon and nitrogen ions are presented in Fig. 2.

A drastic increase of hardness takes place at a dose of 1.10^{16} cm^{-2} both for the films implanted with C^+ and

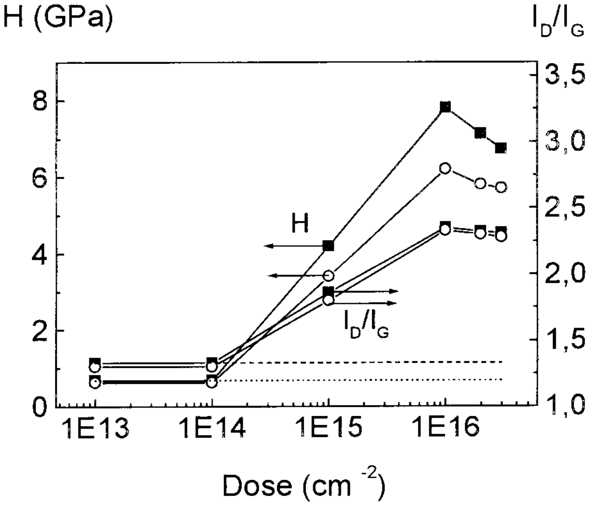

Fig. 2. Hardness (*H*) and I_D/I_G dose dependences for a-C:H films implanted by carbon (■) and nitrogen (●) ions.

N^+ ions. The I_D/I_G ratio dependence on implantation dose changes similarly to hardness (see Fig. 2). Such correlation evidences that hardness increase is connected with the ion-beam induced film disordering. It is interesting to note that despite the fact that the carbon ion mass is less than the nitrogen one the hardness turns out to be higher for the carbon implanted films (Fig. 2). It may be due to the fact that nitrogen containing voids are formed in the nitrogen implanted region.

High dose ($D = 1.10^{17}$ cm^{-2}) nitrogen implantation leads to the appearance of structural inhomogeneities in the implanted region of a-C:H film (Fig. 3).

It should be noted that in the film implanted at doses up to 5.10^{16} cm^{-2} the above mentioned inhomogeneities were not observed. The Raman and microhardness measurements were carried out in the unimplanted region (initial film), in the implanted homogeneous region (reg. 1), and in the region of inhomogeneities (reg. 2). These regions are indicated in Fig. 3 by arrows.

The hardness of initial films depended on deposition conditions, in particular, on bias voltage (see Figs. 2 and 4). Fig. 4 shows the dependence of the hardness on the penetration depth of the indenter (PDI).

It is seen from Fig. 4 that the initial film hardness only slightly depends on PDI. The hardness of the implanted film in the region of structural inhomogeneities drastically differs from the one in the homogeneous region. In reg.1 the hardness initially inreases slightly and then decreases when PDI becomes close to the ion mean projective range (R_p) (see Figs. 3 and 4). As mentioned above, this effect may be connected with microvoid creation during high dose nitrogen implantation and, as a result, swelling of the implanted layer. As is seen from the Fig. 4 the film hardness in region 2 exceeds by more than 2–3.5 times the hardness in region 1 at low PDI (up to 100 nm). At PDI of 150–250 nm the film hardness in region 2 increases and exceeds the hardness in region 1 by more than 5–6 times. It should be noted that the I_D/I_G ratio measured from the initial film and region 1 was 1.81 and 2.94, respectively. At the same time, I_D/I_G for region 2 was 2.6. This seems contrary to the correlation between hardness and I_D/I_G ratio (see Fig. 2). The only way to explain such a contradiction is to suggest that a part of distorted sp^2-coordinated C–C bonds are converted to sp3-coordinated ones. It is evident that the latter must lead to an increase of hardness and to a decrease in I_D/I_G ratio. The structural inhomogeneities in ion implanted a-C:H film can be formed due to existance of local mechanical stresses in the substrate and, as a result in a-C:H film. The stresses can enhance the nitrogen diffusion coefficient in local regions of a-C:H film and inhibit the nitrogen accumulation and voids formation in the implanted layer. On the other hand, the stresses can promote ion-beam induced conversion of sp^2-coordinated bonds in sp^3-coordinated ones [12].

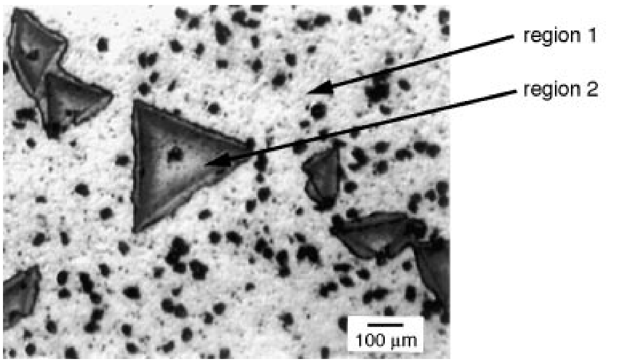

Fig. 3. Optical micrograph of nitrogen implanted a-C:H film ($D = 1.10^{17}$ cm^{-2}).

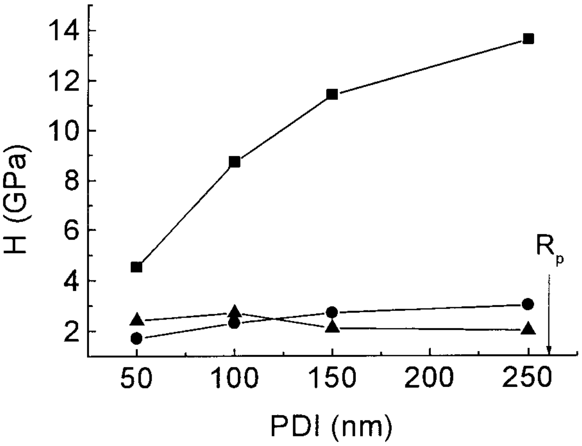

Fig. 4. Dependences of the a-C:H film hardness (H) on penetration depth of indenter (PDI): ●-initial (unimplanted) film; ▲-region 1; ■-region 2. R_p—mean ion projective range (N^+, $E = 150$ keV, $D = 1.10^{17}$ cm^{-2}).

4. Conclusions

Results show that the dramatic increase of the hardness of the films implanted by carbon or nitrogen ions at intermediate doses (up to 3.10^{16} cm^{-2}) derives from ion-beam induced film disordering. At the same time, implantation of nitrogen ions at the dose of 1.10^{17} cm^{-2} leads to the appearance of structural inhomogeneities in a-C:H film. The film hardness in the region of inhomogeneities is extremely high in comparison with the homogeneous region. The effect observed is caused by the ion-beam induced compaction of the film accompanied by conversion of a part of sp^2-coordinated bonds into sp^3-coordinated ones.

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